We cannot imagine life without colour. Colour can be imparted to the particular object by using various types of dyes. They may be Natural of Synthetic origin. Natural dyes are dyes or colorants derived from plants, invertebrates or minerals. The majority of natural dyes are vegetable dyes from plant sources – roots, berries, bark, leaves, and wood — and other organic sources such as fungi and lichens. Archaeologists have found evidence of textile dyeing dating back to the Neolithic period. In China, dyeing with plants, barks and insects has been traced back more than 5,000 years. The essential process of dyeing changed little over time. Typically, the dye material is put in a pot of water and then the textile fibers/yarns to be dyed are added to the pot, which is heated and stirred until the colour is transferred. Textile fiber may be dyed before spinning (dyed in the wool), but most textiles are yarn-dyed or piece-dyed after weaving. Many natural dyes require the use of chemicals called mordents to bind the dye to the textile fibers; tannin from oak galls, salt, natural alum, vinegar, and ammonia from stale urine were used by early dyers.

The discovery of man-made synthetic dyes in the mid-19th century triggered the end of the large-scale market for natural dyes. Synthetic dyes, which could be produced in large quantities, quickly superseded natural dyes for the commercial textile production enabled by the industrial revolution.

Most of the industries use dyes and pigments to colour their products. Among various industries the biggest consumers of dyes are textile, tannery and paper industry. Similarly, dyeing and printing industries uses various types of dyes to impart colour on fabric. The textile industry utilizes large volumes of water in its wet processing operation, and thereby, generates substantial quantities of waste water. While manufacturing dyes and dye intermediates, waste water is generated in significant amount. This is important point, since waste water is the principle route by which dyestuff enters into the environment. For example, of the 450,000 tons of dyestuffs produced in 1978, 41,000 tons were lost to waste streams from textile processing operations and 9000 tons constitute the estimated loss from dye manufacturing facilities. As far as the cost parameters is concerned, it is beyond question that avoiding, or at least minimizing, and reusing effluent is preferable to waste water

treatment, as direct or indirect discharge of waste water certainly changes the water quality of the receiving body.

Collection of basic information on production, water consumption, waste water generation from dyes, dye intermediates manufacturing industries and textile dyeing and printing industries.

Present study is taken up on the dyes manufacturing units, dye intermediates manufacturing units and textile dyeing and printing units. This study has been undertaken to understand the pollution problems faced by the industries manufacturing dyes, dye intermediates and dyeing and printing units of Sachin industrial area.

The production capacity of dyes and dye intermediates manufacturing units is about 4 metric tons / month depending on their production capacity. These units work for about 330 to 340 days per year. While, the textile processing units of Sachin area have an average production capacity of about 40,000 to 1,00,000 meters per day depending upon their production capacity.

The raw materials required for manufacturing of dyes and dye intermediates are oleum, sulphuric acid, hydrochloric acid, α - naphthol, β-naphtol, caustic soda, soda ash,sodium nitrite, liquor ammonia, ammonium sulphate, benzene and its derivatives like phenol, aniline, chlorobenzene etc.

While the necessary raw material for textile dyeing and printing units is man made art silk (polyester) cloth commonly name as "grey". This is obtained from the weavers. The job work is done for dyeing and printing of this grey cloth. Other raw materials required for the processing of art silk cloth are dyes, caustic soda, printing gum, acetic acid, sodium hydrosulphite and other auxiliaries.

The quantity of water consumed per day for dye and dyes intermediate industries varies from 5 KL /day to 30 KL/day. For an industry that consumes water 30 KL/day, the water is used in following manner:

(I) for process : 20 KL/day
(II) for cooking : 2 KL/day
(II) for domestic : 2 KL/day
(IV) for boiler : 6 KL/day

While, the water consumed per day for textile dyeing and printing units varies from 880 KL/day to 2200 KL/day. For an industry that consumes water of 880 KL/day, the water is used in following manner:

(I) for process, cooling and water treatment : 774KL/day
(II) for floor wash : 30 KL/day
(III) for domestic : 5 KL/day
(IV) for boiler : 71 KL/day

The amount of waste water generated by dyes and dye intermediate industry ranges from 2 KL/day to 18 KL/day, while the amount of waste water generated by textile dyeing and printing units ranges from 780 to 1950 KL/day.

Source of samples and frequency of sample collection and detailed study of manufacturing process

The present study can be prented in two parts, the first part of this study can be termed as "Initial study", which was carried out to identify initial details of industries like their production capacity, source of water, water consumption, present effluent treatment and disposal scheme. In this study, it was found that the present effluent scheme is resulted in the generation of high volume of sludge, industries were facing problems in the disposal of this sludge.

The second part of this study can be termed as "Detailed study", which was carried out to study manufacturing process in detail and to identify sources of effluent generation at various stages of manufacturing process. This study was carried out to identify effluent streams which are having similar characteristics, so that effluent having similar characteristics can be segregated and mixed, and can be treated effectively. It was found that effluent was mixed by the industries from all the effluent sources at one place, which makes it difficult to establish effective effluent treatment.

For present study, untreated samples were collected from 10 different dyes and dye intermediates and 10 different textile dyeing and printing industries of Sachin industrial area.

Table -1 Details – type of industries and their products

Industry	Type of Industry	Products
Industry – 1	Dye intermediate manufacturing	Schaeffer's Acid, K Acid, Sulfo Tobias Acid
Industry – 2	Dye intermediate manufacturing	G Salt, Sulfo Tobias Acid
Industry – 3	Dye intermediate manufacturing	Schaeffer's Acid, G Salt
Industry – 4	Dye intermediate manufacturing	G Salt, Amino G Salt, K Acid
Industry – 5	Dye intermediate manufacturing	Sulfo Tobias Acid, Schaeffer's Acid
Industry – 6	Dye intermediate manufacturing	Aniline 2:5 di sulphonic acid, Sulfo Tobias Acid
Industry – 7	Dyes manufacturing	Acid Dyes, Direct dyes
Industry – 8	Dyes manufacturing	Acid Dyes, Solvent dyes
Industry – 9	Dyes manufacturing	Solvent Dyes
Industry – 10	Dyes manufacturing	Reactive Dyes, Direct Dyes

For initial study, the untreated effluent samples from each industry were collected three times a year during year 2010. For detailed study, segregated effluent samples were collected three times a year during year 2011. For the study of characterization and treatment of segregated wastewater, samples were collected during year 2012.

The characteristic parameters of the polluted waste water were determined according to the standard procedures described in the standard methods i.e APHA and IS standards samples were preserved after sampling as tabulated below:

Table -2 Waste water sample parameters with preservation methods

Sr. No.	Parameters	Method for sample preservation
1	pH	Measure within 0 to 4 hours
2	Chemical Oxygen Demand (COD)	Add H_2SO_4 (1:1) to pH 2, and refrigerate at 4 ^{0}C.
3	Biochemcial Oxygen Demand (BOD)	Store at 4 ^{0}C temperature, analyze as soon as possible
4	Total Dissolved Solids (TDS)	Store the sample at 4 ^{0}C.
5	Suspended Solids (SS)	Store the sample at 4 ^{0}C.
6	Chloride	Store the sample at 4 ^{0}C.
7	Ammonical Nitrogen	Store the sample at 4 ^{0}C.
8	Phenolic Compounds	Acidify with H_3PO_4 to pH 4, and add 1 gm $CuSO_4.5H_2O$ per liter of sample
9	Hexavalent Chromium	Acidify with HNO_3 to pH 2, store at 4 ^{0}C.
10	Total Chromium	Acidify with HNO_3 to pH 2, store at 4 ^{0}C.
11	Nickel	Acidify with HNO_3 to pH 2, store at 4 ^{0}C.
12	Oil and Grease	Add 5 ml H_2SO_4 (1:1) per liter of sample.

Waste water samples were collected from equalization tanks of selected industries. Each sample was analyzed for the parameters listed in Table-2 above. The analysis results for dyes and dye intermediate industries show that pH values range from 1.04 to 5.12, COD values range from 35200 to 88500 mg/L, BOD values range from 6600 to 16700 mg/L, TDS values range from 95500 to 180240 mg/L, SS values range from 6950 to 14800 mg/L, Chloride values range from 25500 to 150000 mg/L, Ammonical Nitrogen values range from 52 to 180 mg/L, Phenolic compound values range from 47 to 80 mg/L, Hexavalent chromium values range from 0.012 to 0.204 mg/L, Total Chromium values range from 0.048 to 4.258 mg/L, Nickel values range from 0.01 to 0.02 mg/L. while the results for textile dyeing and printing industries shows that pH value range from 7.24 to 8.92, COD values range from 802 to 1002 mg/L, BOD

values range from 310 to 510 mg/L, TDS values range from 4750 to 7500 mg/L, SS values range from 102 to 195 mg/L, Chloride values range from 2850 to 4100 mg/L, Ammonical Nitrogen values ranges from 82 to 105 mg/L, Phenolic compound values range from 0.25 to 0.57 mg/L, Hexavalent chromium values range from 0.024 to 0.104 mg/L, Total Chromium values range from 0.092 to 0.212 mg/L, Nickel values range from BDL to 0.017 mg/L. It is observed that waste water collected from dyes and dye intermediate manufacturing industries have high COD, BOD, TDS, oil and grease and phenolic compounds, the waste water also contains very low amount of heavy metals like chromium and nickel, the waste water collected from the textile dyeing and printing industries also having high COD, BOD and TDS values but the values of the same are very low as compared to the dyes and dye intermediate manufacturing industries' waste water. On the other side the quantity of waste water generated from the textile dyeing printing industries is very high as compared to the dyes and dye intermediates.

However, there are two Common Effluent Treatment Plants (CETPs) for Sachin GIDC area. All industries selected for this study are member of either of these CETPs, as one CETP receives effluent from only textile dyeing and printing industries, while another CETP receives effluent from dyes and dye intermediate industries. Members of the dyes and dye intermediate CETP are sending their waste water after giving primary treatment (i.e. bringing pH value of the waste water to Neutral). It was observed that large amount of sludge was generated during neutralization of the waste water. Both of the CETPs are located nearby each other in Sachin Industrial area. Waste water was collected during 3 times a year from equalization tank of dyes and dye intermediate industries and mixed in a pre-calculated ratio. 1L of this combined and equalized effluent was given primary treatment with 10% solution of hydrated lime and 5% solution of Ferrous Sulphate. pH of effluent was raised to 11 to 12 with lime solution and neutralized to bring 7 to 8 pH value with Ferrous Sulphate solution. This treatment generates chemical sludge which was filtered by a filter cloth and kept in an oven for drying at 70 ^{o}C for 24 hours. After drying this sludge was collected and weighed. The treated waste water was analyzed for the same parameters of untreated waste water. The volume of sludge generated was found in the range of 482 to 502 mg/L.

Water resources are drastically reducing and the discharge norms are getting stringent day by day, government agencies like MoEF and CPCB are encouraging industries to reduce waste water either by recycling or any other process changes. Considering the quality and quantity of waste water generated from the industries located in the GIDC, Sachin, it was decided to carry out a study which can help industrialist and environmentalists to plan a recycling based treatment system at Sachin GIDC.

After studying manufacturing process of dye intermediates, manufactured at industrial unit of Sachin GIDC, it was found that four stages are involved in the process of dye intermediate manufacturing these are: 1) Sulphonation, 2) Drawing 3) Filtration and 4) Centrifuge. The effluent generated is from 1) Filtration and 2) Centrifuge. The manufacturing process also indicated that during manufacturing of all products involves sulphonation but while Schaeffer's Acid, G Salt and Amino G Salt products utilizes either ammonia liquor or caustic flakes during isolation stages. So the effluent generated from filtration and centrifuge stage will be mild acidic streams, while K –Acid, Sulfo Tobias Acid and Aniline 2:5 Di Sulfonic acid are isolated by pouring reaction mass on Ice bath, therefore the waste water stream from these products will be having highly acidic stream. Therefore it was decided to collect effluent streams generated from each product, regardless to manufacture at same industry or not, and two product groups were formed as tabulated below:

Table -3 Industry wise products

Product group	Products
Product Group – 1	Schaeffer's Acid, G Salt, Amino G Salt
Product Group – 2	K –Acid, Sulfo Tobias Acid, Aniline 2:5 Di Sulfonic acid

Effluent generated from Product group -1 and product group -2 were collected from Filtration stage and Centrifuge stages. Effluent was collected from all industries and then it was mixed product group wise, based on ratio identified from manufacturing capacity and effluent quantity of each industry.

Manufacturing process of dyes produced by industrial unit was studied. It was found that the dyes manufactured are Azo dyes and which is produced by coupling of dye

intermediates. Effluent was generated from filtration / centrifuge stages of dye manufacturing process. The effluent collected from each industry from filtration/centrifuge stage was mixed in a predefined ratio calculated from effluent contribution of each industry.

However, from all industries (dyes intermediate, dyes manufacturing industries, textile dyeing and printing industries) effluent is also generated from utilities like boiler, cooling tower and while washing of reactors, spillages etc., this stream was collected from each industries and was mixed based on ratio identified from manufacturing capacity and effluent quantity of each industry.

This study clearly showed that effluent can be segregated at source and mixed, based on its characteristics, this will eliminate consumption of high volume of treatment chemicals and raw water. Following streams were identified:

Stream -1 Waste water sample collected from filtration and centrifuge stage from Product Group -1 industry

Stream -2 Waste water sample collected from filtration and centrifuge stage from Product Group -2 industries.

Stream -3 Waste water samples collected from filtration and centrifuge stage from dyes manufacturing industries.

Stream -4 Waste water samples collected from boiler, cooling and washing streams from dyes and dye intermediate manufacturing industries

Stream -5 Waste water samples collected from textile dyeing and printing industries.

Treatment of segregated waste water:

It was observed that during stream wise segregation waste water characteristics were almost identical during a whole year, as the streams for segregation was identified after studying the products manufactured by each selected industries. The manufacturing process of each product and the possible characteristics of the waste water generated from each industry were also studied.

Considering above facts, following were decided:

a) Mix Stream -3, Stream -4 and stream -5 and give primary treatment followed by secondary treatment with activated sludge process and tertiary treatment with Fenton reagent., this effluent than passed through lab scale sand and carbon filter and then was analyzed. The analysis results is represented in below table:

Table -4 Characteristic of mixed waste water stream after tertiary treatment

No.	Parameters	Unit	Tertiary treated wastewater
1.	pH	pH Unit	8.11
2.	Chemical Oxygen Demand	mg/L	175
3.	Biochemical Oxygen Demand	mg/L	28
4.	Total Dissolved Solids	mg/L	1960
5.	Suspended Solids	mg/L	7
6.	Chloride	mg/L	2020
7.	Ammoniacal Nitrogen	mg/L	5
8.	Phenolic Compounds	mg/L	0.24
9.	Hexavalent Chromium	mg/L	BDL
10.	Total Chromium	mg/L	0.09
11.	Nickel	mg/L	BDL
12.	Oil & Grease	mg/L	1.05

Note: BDL = Below Detection level

b) Waste water stream of Product group -2, can be used to produce ferrous sulphate by addition of Iron. For this the waste water needs to be checked for pH and acidity only.

Table -5 Quantity of iron scrap required to produce ferrous sulphate from stream -2 waste water.

No.	Particulars	Unit	Amount
1	Quantity of waste water (stream -2)	Liter	2.0
2	Quantity of Iron Scrap consumed	Gram	704
3	Final quantity of waste water stream (i.e. ferrous sulphate slurry)	Liter	2.248

This slurry can be directly used to provide primary as well as tertiary treatment to the mixed stream a) above.

c) Waste water of Stream -1 can be subjected to evaporation considering its high COD and TDS value, which can neither mixed with mixture of streams as suggested in section a) above, which will increase TDS level significantly and ultimately create difficulties in activated sludge process and recycling.; nor can be mixed with waste water stream of Product group -2, which will result in reduction of acidity and will inhibit reaction to produce ferrous sulphate so it was decided that process effluent generated from product group -1 of dye intermediates manufacturing unit needs to be treated with distillation / evaporation system.

Table -6 Quantity of distilled water and solid residue generated from evaporation of Stream -1waste water.

No.	Particulars	Unit	Amount
1	Quantity of waste water (Stream -1)	Liter	0.5
2	Quantity of solid waste remaining	Gram	65.2412
3	Final quantity of waste water stream (i.e. condensate water recovery after distillation)	Liter	0.45

During this treatment, distilled water will be generated which is having high purity and can be used in critical operations of manufacturing process. After distillation /evaporation, the solid material generated can be reused or disposed off to TSDF site.

Suggested Treatment Scheme:

The study also confirms that it is possible to recycle effluent and the treated effluent can be reused for different manufacturing stages, which ultimately reduces the waste water discharges and ultimately helps to conserve precious fresh water resources.

Process effluent generated from product group -2 of dye intermediates manufacturing units can be collected and analyzed for its acidity, based on acidity the entire effluent

can be sold as Spent acid to end users. If the acidity is lower, then the effluent can be treated with waste iron to produce ferrous sulphate which can be used as effluent treatment chemicals and resulting effluent can be treated along with either product group-1 effluent for evaporation. During this recycling process due to implementation of segregation, by-products like Ferrous sulfate, Spent acid were recovered, which are potential sources of income for such centralized facility.

Entire utility effluent (i.e. Effluent generated from boiler, cooling tower) generated from dye intermediate manufacturing industry can be mixed with textile dyeing and printing industry effluent and dyes manufacturing industry effluent and can be treated in conventional CETP, which is operational at Sachin industrial area. For this purpose process modification, i.e. installations of tertiary treatment units at present CETP of Sachin industrial area.

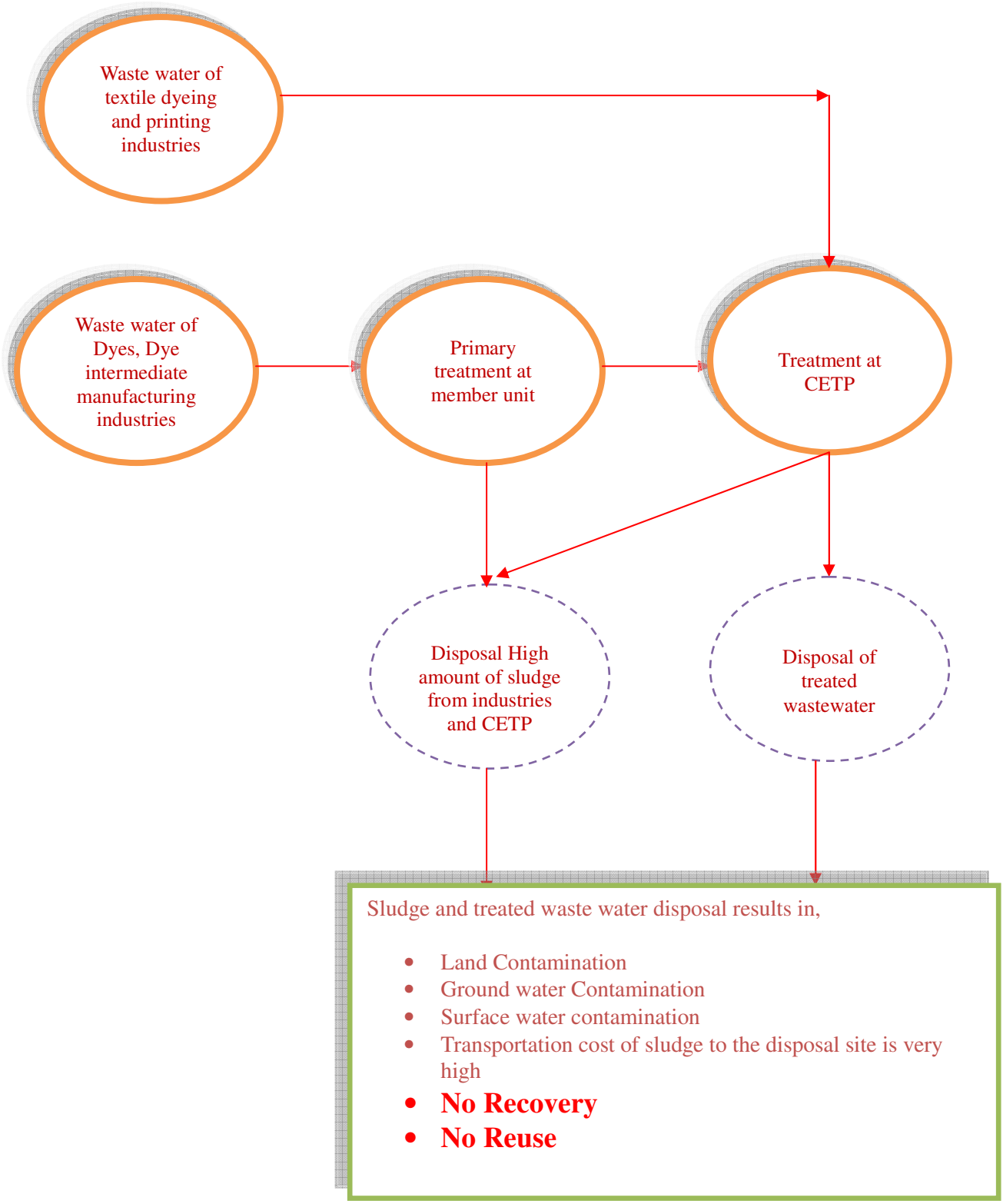
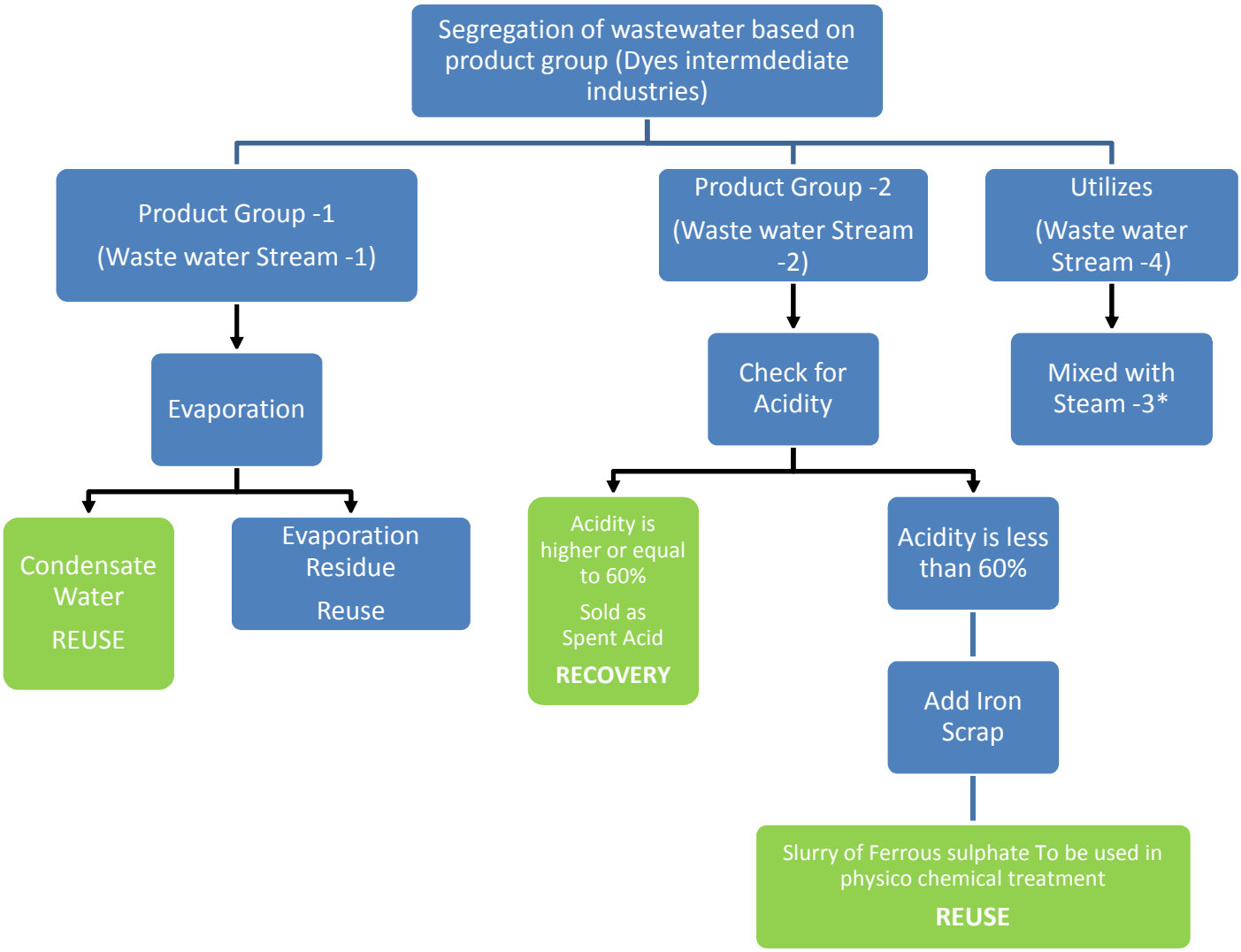

Waste water of textile dyeing and printing industries
Waste water of Dyes, Dye intermediate manufacturing industries
Primary treatment at member unit
Treatment at CETP
Disposal High amount of sludge from industries and CETP
Disposal of treated wastewater
Sludge and treated waste water disposal results in,
Land Contamination
Ground water Contamination
Surface water contamination
Transportation cost of sludge to the disposal site is very high
No Recovery
No Reuse

Figure -1 Present Treatment Scenario at GIDC Sachin



***Note: Further treatment of Stream- 4 is shown in Figure -3**

Figure -2 Proposed Solution: Waste water stream segregation, treatment and recycle (PART -1)

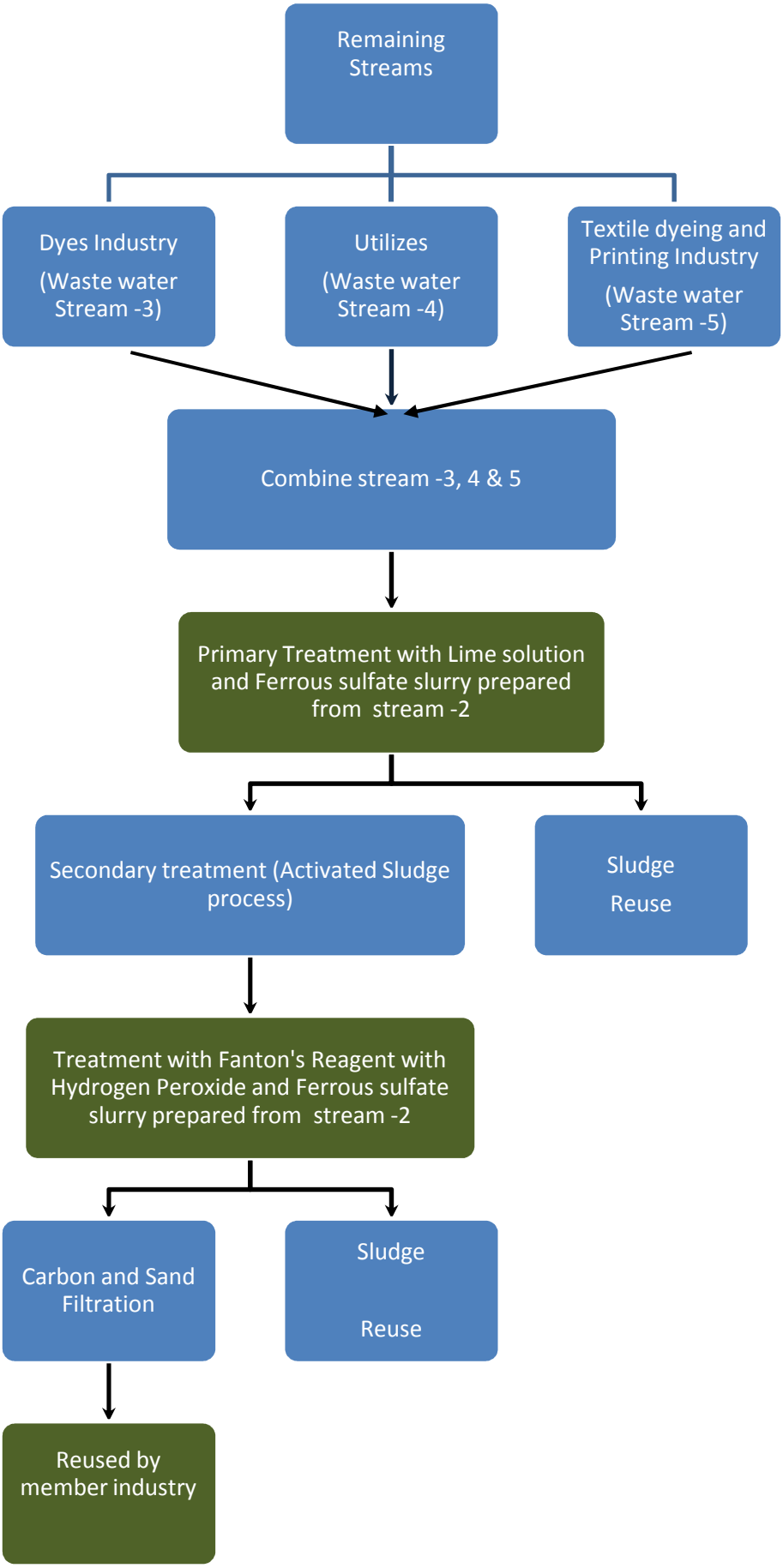

Remaining Streams
Dyes Industry (Waste water Stream -3)
Utilizes (Waste water Stream -4)
Textile dyeing and Printing Industry (Waste water Stream -5)
Combine stream -3, 4 & 5
Primary Treatment with Lime solution and Ferrous sulfate slurry prepared from stream -2
Secondary treatment (Activated Sludge process)
Sludge Reuse
Treatment with Fanton's Reagent with Hydrogen Peroxide and Ferrous sulfate slurry prepared from stream -2
Carbon and Sand Filtration
Sludge Reuse
Reused by member industry

Figure -3 Proposed Solution: Waste water stream segregation, treatment and recycle (PART -2)

This treatment scheme can be financially beneficial to the industries as well as the CETP as little modification is required at member industries level and at CETP level, and the implementation of this scheme can generate revenue by means of sale of Ferrous sulfate, spent acid and recycling of waste water, recovery and reuse of sludge.

Naik Dhaval Jitendrabhai

Dr.Hemangi Desai
Ph. D. Guide